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TECHNICAL NOTE

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THE HOT-PRESSING OF HAFNIUM CARBIDE

(MELTING POINT, 7030° F)

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON

August 1960

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SUMMARY

An investigation was undertaken to determine the effects of the hot-pressing variables (temperature, pressure, and time) on the density and grain size of hafnium carbide disks. The purpose was to provide information necessary for the production of high-density test shapes for the determination of physical and mechanical properties. Hot-pressing of -325 mesh hafnium carbide powder was accomplished with a hydraulic press and an inductively heated graphite die assembly. The ranges investigated for each variable were as follows: temperature, 3500° to 4870° F; pressure, 1000 to 6030 pounds per square inch; and time, 5 to 60 minutes.

Hafnium carbide bodies of approximately 98 percent theoretical density can be produced under the following minimal conditions: 4230° F, 3500 pounds per square inch, and 15 minutes. Further increases in temperature and time resulted only in greater grain size.

INTRODUCTION

The melting point of hafnium carbide (HfC), 7030° F (ref. 1), is the highest reported for any metal or simple metal compound. Because of its high melting point, HfC has frequently been included in tabulations of materials that are potentially useful for structures to operate at very high temperature. Despite this, a search of the literature indicates that relatively little research has been devoted to this material. In particular, no evidence of the production of high-density bodies was found. In discussion with HfC powder suppliers it was indicated that the best bodies produced to date have on the order of 20-percent porosity. By analogy with other ceramic systems, such bodies can be expected to be quite weak and not indicative of the strength capabilities of the material. The purpose of this investigation was to study the processing variables so that conditions for the production of sound specimens for mechanical and physical tests could be established.

As is true for most high-melting materials, HfC is produced in powder form. There are two conventional methods by which these powders are coalesced into a dense solid. These are by cold-compacting the powders and heating, or sintering, them at very high temperatures (generally on the order of 60 to 80 percent of the melting point); and by hot-pressing. The latter method consists of the simultaneous application of a compacting load and heat.

In preliminary experiments performed prior to this study, attempts were made to obtain high-density bodies by the cold-press and sinter method. The best bodies that could be produced still contained about 10-percent porosity. These were produced by compacting at 30,000 pounds per square inch and sintering at 5000° F for 120 minutes in a vacuum atmosphere. Since this density was considered inadequate, the investigation of hot-pressing was conducted. It was felt that hot-pressing might prove superior, because the load can be applied at a temperature where the particles can be expected to possess some plasticity. The study was made on 5/8-inch-diameter by 1/4-inch-thick disks. The variables studied and their ranges are: temperature from 3500° to 4870° F, pressure from 1000 to 6030 pounds per square inch; and time from 5 to 60 minutes.

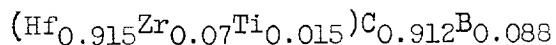
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TEST MATERIAL

The HfC powder (-325 mesh) used in this investigation was supplied by the Carborundum Company. Average particle size was 3.04 microns determined by averaging five Fisher Sub-Sieve Sizer measurements. The chemical analysis is as follows:

	Chemical analysis, weight percent	Theoretical weight percent
Hafnium	89.36	93.7
Combined carbon	6.00	6.3
Free carbon	.03	----
Zirconium	3.45	----
Titanium	.39	----
Boron	.72	----
Total other metal impurities	.05	----

A theoretical density of 12.1 grams per cubic centimeter was calculated for this material based upon the chemical analysis and upon a unit cell dimension of 4.63 angstroms, determined by X-ray diffraction assuming the NaCl-type structure. In making this theoretical density calculation, the zirconium and titanium atoms were assumed to take hafnium atom positions, while boron atoms were assumed to take unfilled carbon atom positions. Also, with these assumptions, the following formula for the hafnium carbide material was determined:



X-ray analysis by Glaser and coworkers, on hafnium carbide prepared by hot-pressing a mixture of the elements, gave a lattice constant of 4.64 ± 0.02 angstroms, leading to an X-ray density, assuming no impurities, of 12.7 grams per cubic centimeter (ref. 2).

APPARATUS AND PROCEDURE

Practical ranges of investigation for each of the hot-pressing variables were established by a series of preliminary hot-pressing trials. These included trials with a double-acting die system. For the thin compacts used in this study, the double-acting die was not found to be advantageous, and its use was discontinued.

To evaluate the effect of each of the three variables, any two were held constant at the approximate mid-range of the investigation while the third was varied through its established range of values. The variable ranges to be investigated are presented in table I. Each entry in this table represents one run.

The hot-pressing dies used in the investigation were fabricated from graphite electrode material, which has high density and good strength for such an application. One end of the die was countersunk for easier extraction of the pressed disk. The anvil, plugs, and plungers made a tight slip fit with the die body to prevent powder leakage. The die assembly is shown in figure 1.

The graphite die was heated by a close-fitting, inductively heated graphite sleeve susceptor. Power was supplied to the 4.75-inch-diameter cooled induction coil by a 200-kilowatt, 3000-cycle-per-second motor generator. The coil was insulated with zirconia and cemented to the water-cooled base plate of a hydraulic press. Excessive oxidation of the susceptor was prevented by the introduction of a continuous flow of helium at the bottom of the coil-susceptor annulus. The assembled die, susceptor, and coil setup are also shown in figure 1.

Temperature was measured with an optical pyrometer that had been calibrated against a National Bureau of Standards certified standard lamp. The temperature measured was that of the outer wall of the die body at the powder charge level. A black-body cavity was approximated by drilling a hole through the graphite susceptor to the die wall. From the hole in the susceptor, an alumina tube was led between two turns of the coil and connected to an Inconel tube with a quartz window at its end. All temperature readings were corrected for the transmission factor of the quartz, and temperature readings were believed to be accurate to $\pm 40^\circ$ F. Fogging of the quartz window was prevented by flowing helium through the sight tube.

After loading the die with 15 grams of HfC and positioning it within the coil, the induction coil power was turned on, a higher than final power setting was made, and the load was applied to the die plunger. In 10 to 20 minutes, depending on the pressing temperature, the power was decreased so that the temperature would level off at the desired value. Final power settings ranged from 40 to 61 kilowatts. At the conclusion of the scheduled pressing time, the load was removed, the power was turned off, and the die was allowed to cool to room temperature. Cooling time was approximately 2 hours.

The hot-pressed hafnium carbide disks were pressed out of the bottom of the graphite die body with a hand-operated arbor press. After removal of all adhering graphite by a belt sander, the density of each disk was determined by weighing in air and in distilled water using an analytical balance. With the technique used, the individual values are generally considered correct within 1 percent. Densities were compared with the computed theoretical density for the powder used. The disks were then mounted in Bakelite, and the circular faces were surface-ground, polished, and heat-tinted. The heat-tinted grains developed varying colors because of the effect of individual grain orientation on the thin oxide films developed during heat-tinting. The structures of the disks were examined microscopically, and photomicrographs were taken using polarized light. In the photomicrographs, the heat-tinted grains vary in color from black to white. All the photomicrographs shown in this report are portions of larger photomicrographs from which grain-size measurements were made. The intercept method (ref. 3) was used to determine the average grain diameter. This method involves counting the number of grains intersected by a line of known length.

RESULTS AND DISCUSSION

As stated previously, the combination of heat and pressure - hot-pressing - favored densification more than the application of temperature alone (conventional sintering). The hot-pressing densification mechanisms are no doubt similar to the mechanisms normally found in sintering. Such mechanisms are used to describe sintering, which is commonly believed to involve three stages.

The first stage involves the welding of particles, is characterized by interconnected voids, and is usually accompanied by very slight grain growth. The second stage is one of densification, in which diffusion proceeds in the presence of the interconnected pores, and which is accompanied by grain growth. This growth is probably the result of grain boundary migration, which proceeds more readily as the contact area between the particles increases. The third stage involves continued diffusion in the presence of isolated pores and is characterized by little further densification. This stage is accompanied by continued grain growth.

Therefore, in hot-pressing, the additional parameter, pressure, increases the formation of local welds between particles by helping to break surface films and by a pressure-bonding mechanism. The increased number of junctions enhances surface diffusion and promotes densification. Then, too, densification may be furthered by plastic flow of the material due to high temperature.

The data obtained in the hot-pressing investigation are shown in table I.

Effect of Temperature at Constant Pressure and Time

The effects of hot-pressing temperatures between 3500° and 4870° F (when pressure and time are held constant at 3500 lb/sq in. and 30 min, respectively) on the density and grain size of hafnium carbide disk compacts are shown by the curves in figures 2 and 3 and the photomicrographs in figure 4. From the curve in figure 2 it can be seen that second-stage sintering (densification) is well in progress at 3700° F. This process is essentially complete at 4200° F, and hafnium carbide disks of approximately 98 percent theoretical density were obtained. An examination of this series of disks with a microscope showed that the number of pores decreases and the pore size increases as pressing temperatures become higher.

After 98 percent of theoretical density was attained at approximately 4400° F, densification was virtually complete. Further increase in temperature did not greatly enhance the density but resulted in rapid grain growth, as indicated by the curve in figure 3 and the photomicrographs in figure 4. Since diffusion increases exponentially with temperature and controls the grain boundary migration, which determines grain size, it would be expected that grain size would increase rapidly with temperature. The grain size of the disk pressed at 4870° F does not fall on the curve in figure 3, probably because the full 3500-pound-per-square-inch load was not applied. This may be due to the plastic deformation of the graphite die parts that occurred at 4870° F, as was evidenced by "mushrooming" of the die plunger. Recession of the die wall was also indicated by the increased disk diameter.

It has been reported that hafnium carbide absorbs carbon at high temperatures (ref. 4), and that a possible eutectic between hafnium carbide and carbon occurs at approximately 5075° F (ref. 5). None of the microstructures showed any signs of liquid formation or of graphite precipitation. To check further the possibilities of carbon pickup by the hafnium carbide, an X-ray diffraction pattern was taken of the polished face of the disk hot-pressed at 4870° F. There was no change in lattice parameter from that of the starting material to indicate solution of carbon.

Effect of Pressure at Constant Temperature and Time

The effects of pressure in the range of 1000 to 6030 pounds per square inch (when temperature and time are held constant at 4230° F and 30 min, respectively) on the density and grain size of hafnium carbide disk compacts are shown by the curves in figures 2 and 3 and the photomicrographs in figure 5.

In figure 2 it can be seen that by holding temperature and time constant at 4230° F and 30 minutes, respectively, density increased from 94 to over 99 percent of theoretical as pressure was increased from 1000 to approximately 4500 pounds per square inch. Pressure above 4500 pounds per square inch did not increase the density further. The increase in density with increasing pressure can be ascribed to enhanced diffusion resulting from improvement of contact between the somewhat plastic particles. Changes in pore size and pore number with increasing pressure were small.

As indicated in figure 3, the effect of pressure on the grain size at the higher load levels becomes less well defined. This may be due to a number of possible mechanisms. The first of these is the fragmentation of the powder particles when the load is applied. Concurrently, the deformation of other powder particles may promote recrystallization at some time during the heating cycle. It may also be that the observed die deformation, as previously described, has proceeded to a point during the run where it would prevent full load application. It is felt that one or a combination of these factors is responsible for the low values of the points at 5200 and 6030 pounds per square inch in figure 3.

Effect of Time at Constant Temperature and Pressure

To determine the effect of time on the density and grain size of hot-pressed hafnium carbide disks, four hot-pressing runs were made. Temperature and pressure were held constant at 4230° F and 3500 pounds per square inch, respectively, and the times investigated were 5, 15, 30, and 60 minutes.

From the curve in figure 2, density can be seen to have its greatest increase when time is increased from 5 to 15 minutes. Above 15 minutes, for which time 98 percent of theoretical density was obtained, increases in density are negligible, and for this temperature and pressure level (4230° F and 3500 lb/sq in.) densification is virtually complete.

The grain size, however, continues to increase with increasing time, as shown by the curve in figure 3 and the photomicrographs in figure 6. This would be expected, since grain-boundary migration, controlled by diffusion, would continue with time at temperature.

With the knowledge of the hot-pressing characteristics of this lot of hafnium carbide, it is now possible to hot-press larger disks or bar shapes 1/4 inch thick to approximately predetermined density and grain size. Other lots of material will undoubtedly differ in composition and grain size, but the relative effects of the hot-pressing variables determined here should still hold true.

CONCLUSIONS

The investigation to determine the effects of the hot-pressing variables (temperature, pressure, and time) on the density and grain size of hot-pressed hafnium carbide disks gave the following major results:

1. Hafnium carbide bodies of approximately 98 percent calculated theoretical density can be produced by hot-pressing at temperatures of about 4230° F when employing a pressure of 3500 pounds per square inch and a time of 15 minutes. Further increases in temperature did not improve density but resulted in an accelerated rate of grain growth.
2. In the range of 1000 to 6030 pounds per square inch, pressure has a small effect on density and grain growth at a temperature of 4230° F.
3. At the operating temperatures and pressures established, densification is essentially complete after 15 minutes, and only grain growth results for longer pressing times.

Lewis Research Center

National Aeronautics and Space Administration
Cleveland, Ohio, May 16, 1960

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TABLE I. - HOT-PRESSING VARIABLES AND RESULTS

	Temp., °F	Press., lb/sq in.	Time, min	Density, g/ml	Theor. density, %	Av. grain-size diam., microns	
						Mean	Standard deviation
Effect of hot- pressing temp.	3500	3500 ↓	30 ↓	9.5	78.5	6.4	0.4
	3680			10.0	82.6	7.2	.6
	3760			10.8	89.3	10.3	.8
	3860			11.2	92.6	12.9	1.1
	4040			11.7	96.7	18.5	1.5
	^a 4230			11.8	97.5	26.4	3.1
	4325			11.8	97.5	24.6	2.0
	4640			11.9	98.3	54.6	6.7
	4870			11.9	98.3	52.3	7.7
Effect of hot- pressing press.	4230	1000	30 ↓	11.4	94.2	17.6	1.4
	↓	1850		11.6	95.9	19.7	1.6
	↓	2750		11.8	97.5	21.9	2.5
	↓	^a 3500		11.8	97.5	26.4	3.1
	↓	4350		12.0	99.2	27.4	2.6
	↓	5200		12.0	99.2	22.0	1.5
	↓	6030		12.0	99.2	22.3	1.1
Effect of hot- pressing time	4230	3500 ↓	5	11.5	95.0	16.1	1.3
	↓		15	11.9	98.3	24.1	1.7
	↓		^a 30	11.8	97.5	26.4	3.1
	↓		60	11.9	98.3	28.2	2.9

^aSame disk.

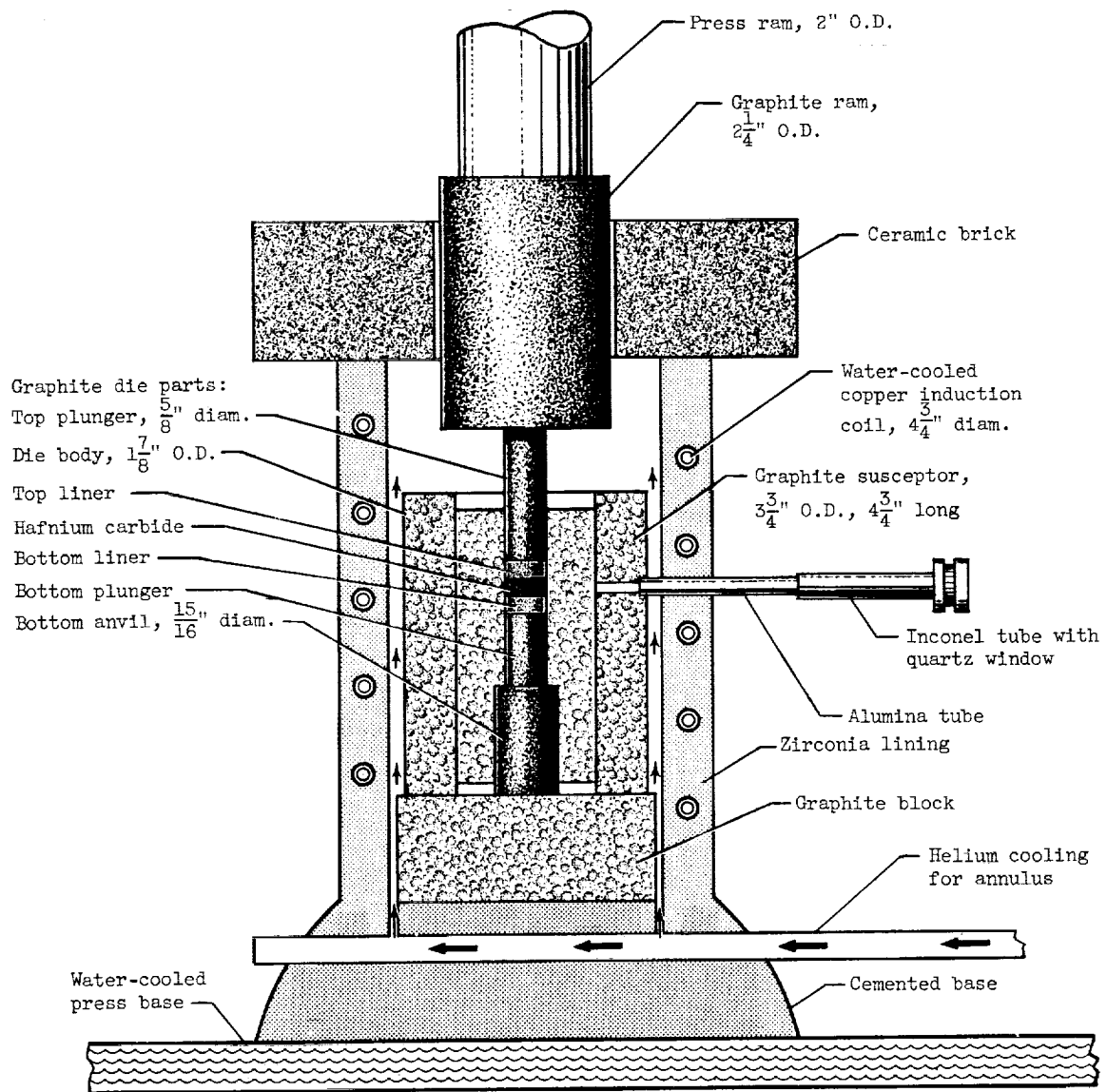


Figure 1. - Hot-pressing apparatus.

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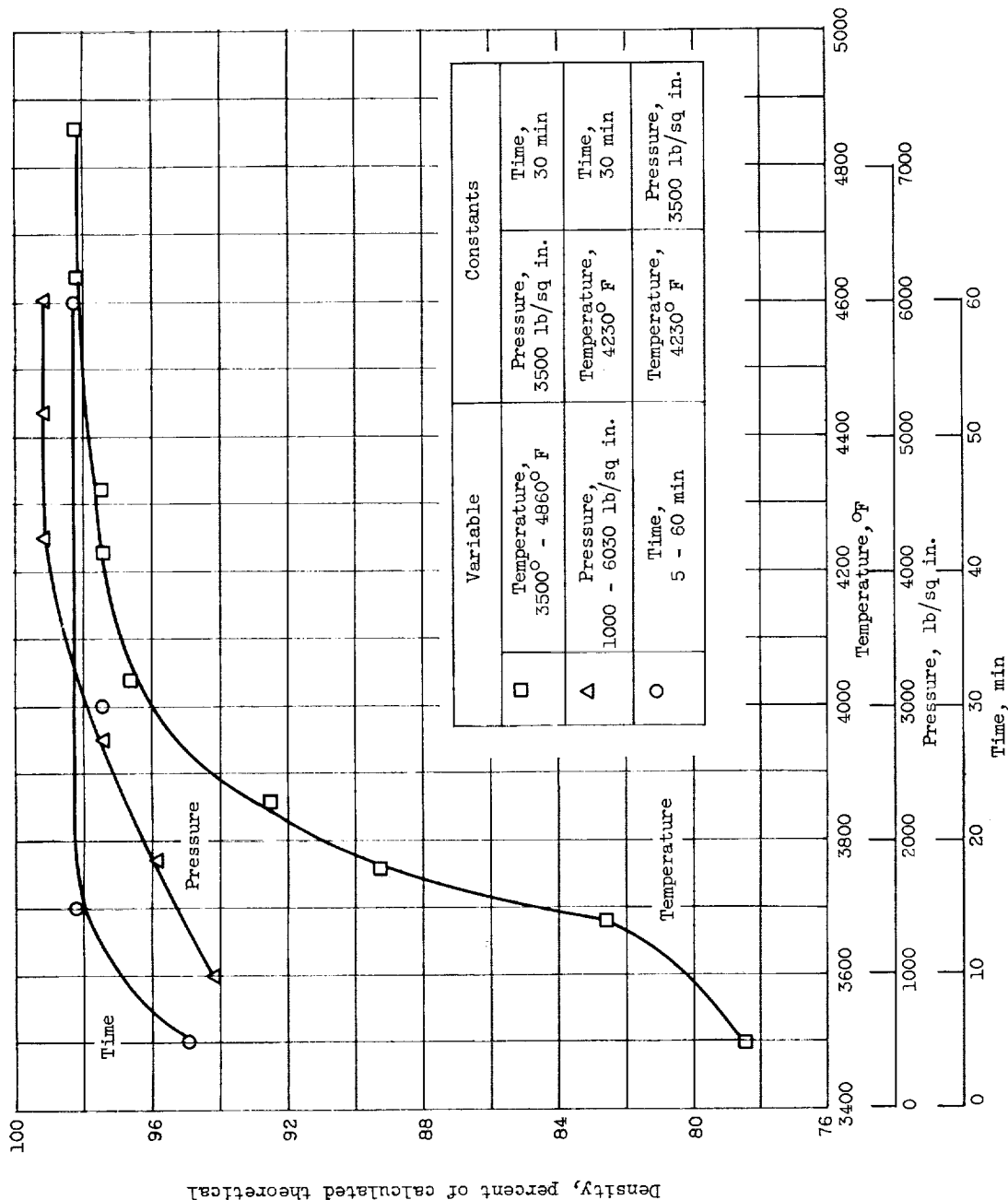
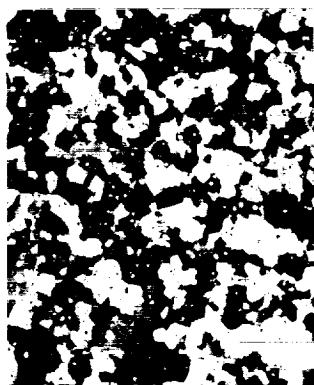
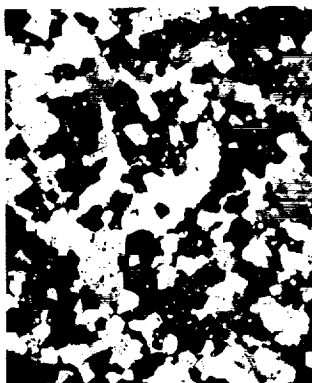


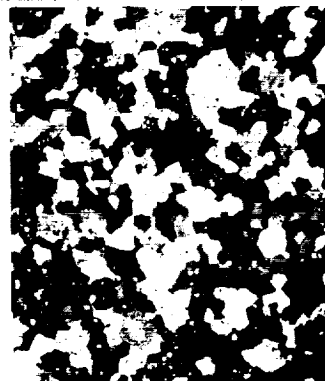
Figure 2. - Variation of density with hot-pressing temperature, pressure, and time.



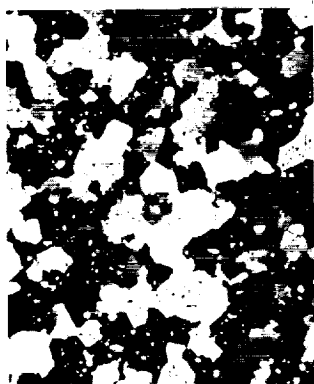
Pressure: 1000 lb/sq in.
Density: 11.4 g/ml
Av. grain diam.: 17.6 microns



1850 lb/sq in.
11.6 g/ml
19.7 microns



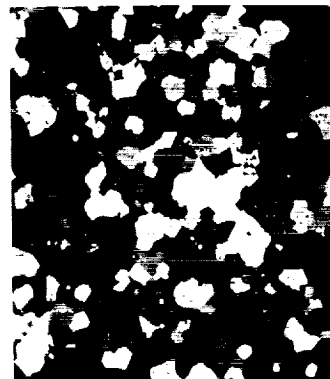
2750 lb/sq in.
11.8 g/ml
21.9 microns



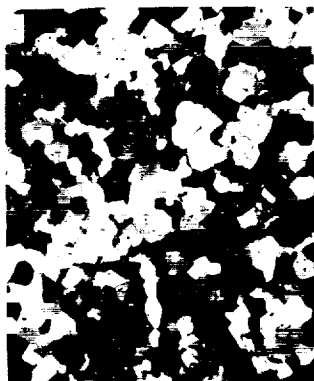
3500 lb/sq in.
11.8 g/ml
26.4 microns



4350 lb/sq in.
11.9 g/ml
27.4 microns



5200 lb/sq in.
12.0 g/ml
22.0 microns

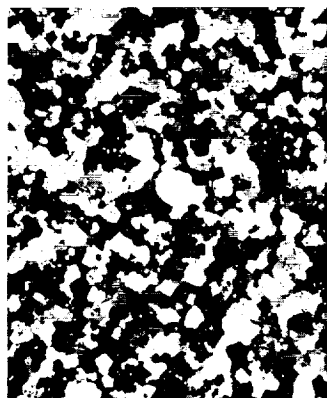


6030 lb/sq in.
12.0 g/ml
22.3 microns

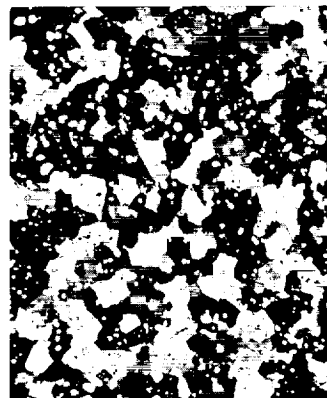
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Figure 5. - Photomicrographs of hot-pressed hafnium carbide disks pressed at 4230° for 30 minutes at pressures indicated. Etch, heat-tint; magnification, X250; illumination, polarized light. (Reduced 62 percent in printing.)

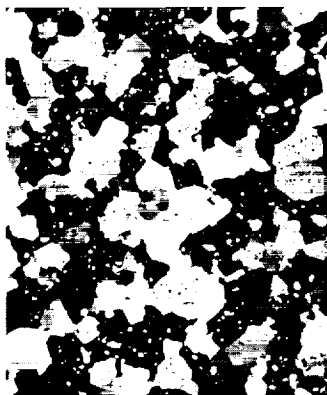
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Time: 5 min
 Density: 11.5 g/ml
 Av. grain diam.: 16.1 microns



15 min
 11.8 g/ml
 24.4 microns



30 min
 11.8 g/ml
 26.4 microns



60 min C-53329
 11.9 g/ml
 28.2 microns

Figure 6. - Photomicrographs of hot-pressed hafnium carbide disks pressed at 3500 pounds per square inch and 4230° F for times indicated. Etch, heat-tint; magnification, X250; illumination, polarized light. (Reduced 62 percent in printing.)

